

Response to Comments

ez-2016-00398y: Legacy and emerging perfluoroalkyl substances are important drinking water contaminants in the Cape Fear River Watershed of North Carolina

From the editor:

MANUSCRIPT FILE:

- Capitalize the article title according to title case.

Corrected as requested.

- Add the corresponding author's telephone number to the title page.

Corresponding author's telephone number was added.

- Replace the blue font color with black throughout the text.

Font color has been changed to all black.

- Reduce the length of the abstract to 200 words (206 words in length at this time).

We shortened the abstract to exactly 200 words.

Commented [DK1]: At 200 now. Check one last time once finalized.

- Remove the label "Table of Contents Graphic" from the TOC graphic on page 3.

We developed a new TOC graphic as requested in the next comment and submitted it in a separate file according to the instructions to authors.

- Create a new TOC graphic that is publication size and does not include any maps.
- Authors should explain how the map in the TOC Graphic was created.

We have created a new TOC graphic without map and in the required size.

- Add a supporting information paragraph, above the references section, in this format:

ASSOCIATED CONTENT

Supporting Information Available: [Add description of your supporting material here.] This material is available free of charge via the Internet at <http://pubs.acs.org>.

Description of SI has been added above the references section as follows:

"Supporting Information Available

The following information is available free of charge via the Internet at <http://pubs.acs.org>:

Six tables, five figures, information about PFASs, analytical methods, and detailed results."

- Include ten author names, then use "et al" in the references.

References has been updated to replace authors beyond ten with “et al”.

- Abbreviate journal titles per CASSI in the references.

The reference has been updated to use journal abbreviations.

- Add the volume number and page range to reference 1.

Volume number and page range have been added to reference 1.

- ES&T Letters discourages the use of sources that are not peer-reviewed—see references 4-6, 15, 28, 29, and 31.

We deleted reference 15 (DuPont web link) and instead refer to peer-reviewed manuscripts that report on GenX properties. The manuscript was changed to “...has been produced since 2010 with the trade name “GenX”. Except for a few studies, (most by the manufacturer),¹⁶⁻²⁰ little is known about the ...” Reference 28 and 29 (30 and 31 in the revised manuscript) are peer-reviewed research reports. References 4-6 and 31 (now 33) are key government reports and data sources forming the basis for regulatory policies in the US and Sweden. In the context of this manuscript, we feel that EPA documents are important primary sources.

Commented [DK2]: Cross-check with final manuscript version in case we delete.

Commented [DK3]: Make sure this is correct when we submit.

Commented [DK4]: Make sure this is correct when we submit.

SUPPORTING INFORMATION FOR PUBLICATION:

- Add the header “Supporting Information” to the top of the title page.

The requested header was added.

- Capitalize the article title according to title case.

Corrected in both the main manuscript and SI.

- Add affiliations 4-6 to the title page.

Affiliations 4-6 were already on the title page.

- Add the corresponding author’s email address and telephone number to the title page.

Corresponding author’s telephone number was added.

- Move the caption for figure 1 to below the figure.

Caption for figure 1 has been moved to below the figure.

- Confirm that permission is not required for the maps used in figure S2 or provide a permission form.

Permissions are not required for the maps used in figure S2. The GIS map layers of NC and the Cape Fear River basin were downloaded from NC OneMap (data.nconemap.gov), an evolving initiative directed by the NC Geographic Information Coordinating Council. It is stated on their website that “Geospatial data content and map services provided directly from the NC OneMap

Geospatial Portal are free to download and use without restriction.” The GIS map layer of the US was also taken from the public domain (US Census Bureau, <https://www.census.gov>).

- *Abbreviate the journal title per CASSI in reference 1.*

The reference style has been updated to use journal abbreviations.

From Reviewer 1

This is an interesting paper. The work is well conducted and the presentation is very good. I only had a few minor comments.

L61. Manufacturers

The typo was corrected.

L63. Are the identities “confidential business information”?

In some cases, yes. We modified the sentence to: “Some fluorinated alternatives were recently identified, but others remain unknown because compounds are either proprietary or manufacturing byproducts.”

L229. Sentence awkward; suggest “...difficulty in effectively removing legacy PFASs and PFECAs...”

The text has been revised as suggested by the reviewer.

Implications of this finding in regards to reuse of treated WWTP effluent directly as drinking water or to recharge drinking water groundwater reservoirs?

In the studied watershed, the only confirmed source of PFECAs is the discharge from a fluorochemical manufacturer. This water would not be a candidate for direct potable reuse or groundwater recharge. Until we gain a better understanding of other PFECA sources, we are reluctant to expand the implications of our findings to direct potable reuse and groundwater recharge scenarios.

Commented [DK5]: Andy wrote: Possibly cite Schymanski et al. [dx.doi.org/10.1021/es4044374](https://doi.org/10.1021/es4044374) Environ. Sci. Technol. 2014, 48, 1811–1818.

Commented [DK6R5]: I don't think this paper is a good fit. Is there another one? Wang et al Environment International papers?

Commented [M7R5]: Wang's paper mentioned “confidential information”, so yes. But can't find one talked about “unintentional byproducts”. Andy and Mark, do you have any suggestions?

From Reviewer 2

The authors capitalize on their newly-discovered perfluoroalkyl ether carboxylates and share insight into the fate of the PFECAs in drinking water and in drinking water treatment. The authors present the first study that examines sorption of the PFECAs to PAC and the removal of the PFECAs during drinking water treatment. The high standards for novelty and significance, as well as technical quality, in Environmental Science & Technology Letters, are met.

1) Comment on the room temperature storage conditions and how the authors confirmed that loss of analyte to the vial during storage was negligible.

Samples were stored in HDPE bottles until processing. We conducted a 70-day holding study with 40 samples and standard solutions at room temperature. The chromatographic peak areas after storage were 1.1 ± 0.1 times of that before storage for all PFAS species in all samples. This information along with the information presented in response to comment 2 of reviewer 2 (below) illustrates that the loss of analyte during storage, which was <7 days for this study, was negligible. We added the following sentence to the manuscript: "PFAS losses during storage were negligible based on results of a 70-day holding study at room temperature."

For analysis, samples and standards were kept in vials on the sampling tray for the length of a typical analysis (less than a day). Complete standard curves were analyzed at the beginning and end of each analysis, and changes over the course of an analysis were negligible.

2) How do the authors know that loss from the batch reactors during adsorption experiments was due to the PAC rather than partitioning to the vial? The reviewer has observed significant loss from the aqueous phase to vial walls during sorption experiments under certain conditions.

We conducted carbon-free blank tests with PFASs spiked into ultrapure water and North Carolina surface water as part of adsorption isotherm experiments that are not reported in this paper. After contact times of 2 and 3 weeks, concentrations were $96 \pm 17\%$ $103 \pm 22\%$ of initially measured concentrations, respectively. These results illustrate that PFAS losses to container surfaces and during mixing at room temperature over a period of 2-3 weeks were negligible. We added the following sentence to the manuscript: "PFAS losses in PAC-free blanks were negligible."

3) How do the authors control for loss during LC-MS/MS analysis? Long-chained PFASs are known to be at the air-water interface or on the vial walls during aqueous phase direct injection.

We processed and analyzed all samples in the same manner as calibration standards and quality control solutions. Thus, any potential losses would be proportional in both standards and samples, leading to automatic correction in concentrations estimates (which is also proved by the 75-125% recovery of

quantify control solutions). Also, we have tried to find compelling evidence of PFAS accumulation at the air-water interface when aqueous PFAS concentrations are in the ng/L range, but we have not seen it. This may be happening in AFFF impacted sites at high concentrations, but not at the PFAS levels observed in our research.

4) Line 30 and throughout: PFASs stand for per- and polyfluoroalkyl substances. Change to per- and polyfluoroalkyl substances (PFASs) or use perfluoroalkyl substances throughout.

We revised the manuscript such that the PFAS acronym stands for per- and polyfluoroalkyl substances.

5) Lines 103-112: State the fraction or percentage of methanol added to each batch reactor when the legacy PFASs are added at 1000 ng/L. A high fraction of methanol can greatly impact partitioning to PAC and other media.

Our primary dilution standard was in methanol and our secondary dilution standard was in water. Based on our spike volume, the methanol content in the reactors was 1 ppm_v. Studies from other groups have shown methanol <0.1% has no effect on adsorption. Also, we conducted adsorption tests with non-spiked surface water to study the removal of native PFECAs. Average PFECA removal percentages obtained in spiked samples were 1.05±0.11 times those in non-spiked samples, when comparing the same PAC dose at the same contact time. We added the following sentence to the manuscript: "Data from spiked and non-spiked experiments showed that the methanol contribution (1 ppm_v) from the primary stock solution and the added legacy PFASs did not affect native PFECA removal."

6) Line 118: Use nmol/L to compare species rather than ng/L since each analyte has a different molecular weight and is therefore not directly comparable.

We think occurrence data should be reported in ng/L, which is more readily understandable than nmol/L. Units of ng/L also link directly to EPA health advisory levels for PFOA and PFOS (70 ng/L).

7) Line 120: State whether the number of carbons corresponds to fluorinated or total since the fluorinated carbons and total carbons are not the same for the PFCAs.

We meant total carbons. The sentence was changed to "PFCAs with 4-8 total carbons" to clarify.

8) The discussion using both mean and median is distracting. Either the median has utility, and should be explained, or omit the median from the discussion.

Presenting both median and mean values has utility. Environmental pollutants typically occur in lognormal distributions, for which the simplest and most appropriate summary statistic is the median. Together, the median and mean

values are useful to assess the skewness of the distribution. In risk assessment, on the other hand, exposure is based on mean daily intake. Thus, in the context of human exposure to PFASs via drinking water, mean values have greater utility. In the end, we decided to eliminate median values from the discussion to provide space for a more detailed discussion about temporal changes in the composition of PFAS homologues (comment 5 of reviewer 4).

9) Line 166: change units to ng/L (typo?)

Yes, it was a typo, and we corrected it to ng/L in the revised manuscript.

10) For Fig. 2b, consider assuming equal molar response for all PFECAs and compute concentrations, accounting for differences in molecular weight, using calibration for PFPrOPrA. Equal molar response assumptions have been used in the quantification of PFASs in the literature. Concentrations have more meaning than area counts. If area counts must be used, demonstrate that concentrations are proportional to area counts.

Our calibration data show that molar response factors for the seven PFCAs were highly variable (RSD of 53%). Thus, we should not assume equal molar responses for all PFECAs and estimate other PFECA concentrations from the calibration curve of PFPrOPrA. Such concentration estimates would be highly speculative and could mislead readers.

11) Lines 183-184: Keep this sentence with the discussion of the 100 mg/L PAC dose rather than switching between doses.

We deleted the sentence that included the 60 mg/L PAC dose to improve flow and to save space to allow us to accommodate additions required to address comments from other reviewers.

12) Line 218: Change to "PFOA, for which it is replacing..."

We disagree that the word "for" is needed here.

13) Lines 226-228: Move to the discussion about Community C for better flow.

We moved the sentence to the section of "PFAS occurrence in drinking water sources" as suggested.

From reviewer 3

The manuscript discusses the presence of legacy and emerging PFASs in the Cape Fear River watershed. The manuscript is based on sound analytical data, representing both the usual suite of legacy PFASs and an emerging group of perfluoroalkyl ether carboxylic acids (PFECAs). Sampling was conducted somewhat haphazardly at 3 DWTPs at different sampling intervals and according to different procedures over varying time scales, representing a total of over 200 samples.

There are several concerns about the manuscript as presently presented.

- 1. All samples were taken in drinking water treatment plants (DWTPs), not in the actual watershed, so the title is somewhat misleading.*

We think using the word “watershed” in the manuscript title is appropriate. Locations for collecting the more than 200 surface water samples coincided with intake locations of 3 DWTPs that were all located in the Cape Fear River watershed. Also, the water sample for adsorption experiments was taken directly from the Cape Fear River and represents a fourth sampling location in the watershed. The definition of “watershed” includes the land representing the catchment basin. This land is home to DWTPs and the residences receiving water treated by these DWTPs.

- 2. There are 3 parallel strands of the manuscript, and they do not link together easily (a) a temporal trend of legacy PFASs that is eluded to in the manuscript (no change to 10 years ago), but not substantiated with a Figure or Table; (b) the lack of removal of legacy or emerging PFASs in the DWTPs; and (c) the presence of emerging perfluoroalkyl ether carboxylic acids in the drinking water.*

This paper focuses on the importance of legacy and emerging PFASs as drinking water contaminants (see manuscript title). To understand the effect of a contaminant on drinking water quality requires knowledge about its occurrence in source water and the ability of treatment processes to remove the contaminant. All three components of our manuscript, i.e. establishing (1) legacy PFAS and PFECA occurrence in the watershed of interest, (2) lack of legacy PFAS and PFECA removal in conventional and advanced drinking water treatment processes, and (3) the effect of ether oxygen incorporation into PFASs on adsorbability by activated carbon, serve this overarching theme.

With respect to the comment regarding no change to 10 years ago, we referenced in the original manuscript a 2007 ES&T paper that contains the data to support this statement. We quantified the statement further in the revised manuscript as follows: “Maximum PFOS and PFOA concentrations were 346 and 137 ng/L, respectively. Similar PFOS and PFOA concentrations were observed in the same area in 2006, suggesting that

PFAS source(s) upstream of community A have continued negative impacts on drinking water quality.”

3. *Personally, I find Figure S4 to be more insightful than some of their current Figures, but this also speaks to the problem of focus for this submission. It is not entirely clear what the focus is.*

The focus of our manuscript is on drinking water quality and treatment. In this context, we feel that the current figures are more relevant than Figure S4. While we use Figure S4 to support our brief discussion on hydrological processes controlling PFAS concentration in source water, the focus of our paper is different as already outlined in our response to the previous comment.

4. *Figure 2 has some repetition of Figure 1, so these 2 could be combined.*

We disagree that information from Figure 1 is repeated in Figure 2. In Figure 1, spatial differences in PFAS concentrations, averaged over time, are shown (mean PFAS concentrations at three DWTP intakes). In Figure 2, PFAS fate after each treatment step in a full-scale water treatment plant is shown for a given sampling date. We think combining the figures would lead to a loss of clarity and hurt the flow of the associated discussion.

Other comments

Figure 3 a – the alignment of the captions is off – place legend at right angle to make it match up.

We changed the axis labels to vertical and adjusted the brackets to achieve the desired alignment as suggested.

Figure 3b – is there another way to plot these data – the authors should see how to combine the curves into a single one – how about trying either Log Kow, aqueous solubility or maybe molar volume here?

The main goal of our analysis was to determine how replacement of CF₂ groups with ether oxygen groups affects PFAS adsorbability. The currently chosen approach allows us to do so, but the approach suggested by the reviewer would not. We did explore the approaches suggested by the reviewer, but in the end, we decided to not include the results in the manuscript or the SI because such approaches should be used for the analysis of equilibrium data. The latter is a topic for a future manuscript.

From reviewer 4

In this manuscript, the authors measured legacy and emerging perfluoroalkyl acids (PFAAs), in particular those overlooked perfluoroalkyl ether carboxylic acids (PFECAs), in three drinking water facilities in the US and tested the efficacy of conventional and advanced water treatment techniques on these substances. This topic is of high international interest, and the manuscript is very timely and mostly well written. Therefore, I would like to congratulate the authors for their important work. However, there are also several points that have room for adjustment/improvement. Therefore, I would recommend the manuscript be accepted for publication after a moderate revision; detailed comments are listed below.

Major comments

1. *The term of “perfluoroalkyl substances (PFASs)” in the title and throughout the manuscript is not entirely accurate, the authors are recommended to use “per- AND POLYfluoroalkyl substances”, as not all PFASs are perfluorinated.*

We revised the manuscript such that the PFAS acronym stands for per- and polyfluoroalkyl substances.

2. *Some details are missing in the manuscript, e.g., how the quantitation limits were determined in this study? In addition, what were the detection frequencies of individual compounds in those samples? Also, I’m not entirely sure about if concentrations < quantitation limits were considered as zero to calculate means and total PFASs is an appropriated approach to treat “non-detects”. It’s certainly very conservative, but I would encourage the authors to consider methods described in this article (<http://pubs.acs.org/doi/pdf/10.1021/acs.est.5b02385>) to handle “non-detects”.*

Regarding the determination of quantitation limits, we added the following to the analytical method description in the SI: “The QL was defined as the first point of the standard curve, for which the regression equation yielded a calculated value within $\pm 30\%$ accuracy.” This is a conventional approach used in many labs in this field. We want to stress that the focus of the paper is the sustained and pervasive elevated concentrations that are observable in this watershed.

We elected to use a value of zero to calculate summary statistics (in place of other approaches such as $LOQ / \sqrt{2}$) in order to provide a conservative estimate of mean concentrations.

The purpose of this paper was to highlight elevated PFAS concentrations in drinking water sources, not to discuss detection frequencies at levels below our QLs. Given the space limitations, it is also not possible to add such a discussion.

3. *I am wondering if the authors would be able to calculate additional emission fluxes of PFPrOPrA from their sampling campaign? This would give readers more perspective how it*

may be translated to total environmental burden. In addition, I am wondering if the authors would be able to compare the measured levels/emission fluxes of PFPrOPrA with those of PFOA at the same place to see if there is an improvement in terms of environmental contamination by the same manufacturer, at least in terms of the amounts of chemicals released.

We did estimate mass fluxes of PFPrOPrA from stream flow and PFPrOPrA concentration data and added the following to the revised manuscript: "Stream flow data were used in conjunction with PFPrOPrA concentration data to determine PFPrOPrA mass fluxes at the DWTP intake of community C. Daily PFPrOPrA mass fluxes ranged from 0.6-24 kg /d with a mean value of 5.9 kg /d." A comparison to PFOA mass fluxes was not possible because we lack sufficient data in 2006.

Minor comments

1. L52: I would suggest changing to "the presence of POINT SOURCES SUCH AS industrial sites", as there are other points sources such as landfills and agriculture fields that are not described here.

The text has been revised to "...the presence of sources such as industrial sites...". We omitted the word "point" because some sources can be non-point sources (e.g. runoff from fields receiving biosolids).

2. L54: "Such as" may not be the best word here, as long-chain PFASs only refer to PFCAs, PFSA and their precursors, but not other PFASs such as PFECAs. I think the authors need to be more specific here.

To address this comment, we revised the text to "...long-chain perfluoroalkyl sulfonic acids ($C_nF_{2n+1}SO_3H$, $n \geq 6$, PFSA) and perfluoroalkyl carboxylic acids ($C_nF_{2n+1}COOH$, $n \geq 7$, PFCA)..."

3. L56: I would suggest removing "ecotoxicological and". As far as I know, ecotoxicological concerns have not been used in the regulatory context of PFASs.

We changed to word "ecotoxicological" to "ecological persistence".

4. L75: There are another two studies on GenX that I know of.

a. Wang, J.; Wang, X.; Sheng, N.; Zhou, X.; Cui, R.; Zhang, H.; Dai, J. RNA-sequencing analysis reveals the hepatotoxic mechanism of perfluoroalkyl alternatives, HFPO2 and HFPO4, following exposure in mice. *J Appl Toxicol* 2016.

b. Gomis, M.I., Wang, Z., Scheringer, M., Cousins, I.T., 2014. A modeling assessment of the physicochemical properties and environmental fate of emerging and novel per- and polyfluoroalkyl substances. *Sci. Total Environ.* 505, 981–991.

The references have been added to the manuscript and the text has been revised to "...except for very few studies...".

5. L125-126: *I'm not sure about the statement "suggesting that PFAS source(s) upstream of community A have LONG-TERM negative impacts on drinking water quality". This gives me the impression that the impacts of these sources are long-term. But could it be that there are just continuous source(s) upstream of community A? The impacts may be short-term, but as source(s) are still ongoing, so there are still impacts on drinking water quality? I'm also wondering if the measurements today and ten years ago have the same homologue patterns? This would be another interesting point to explore if there were any source shift upstream.*

We agree with the first comment and changed "long-term" to "continued".

In response to the question about homologue patterns, we added the following discussion to the revised manuscript: "It is important to note, however, that the contribution of long-chain PFACs to Σ PFAS shifted from long-chain (70% $C_nF_{2n+1}COOH$, $n \geq 7$) in 2006 to short-chain (70% $C_nF_{2n+1}COOH$, $n=3-6$) in 2013. In contrast, the PFOS contribution to Σ PFAS remained the same (13%)."

6. L127-128: *This statement is not so correct. Even the production has been phased out in the US RECENTLY, there may still be enough products in use that were manufactured prior to the phase-out. A delayed decrease of environmental levels in response to production phase-out should always be expected. Therefore, the sentence here needs to be reformulated to reflect this expected delay.*

We edited the sentence slightly to: "Also, our data show that legacy PFASs remain as surface water contaminants of concern even though their production was recently phased out in the US." This sentence is a factual observation. Given the space limitations, we decided to refrain from speculating why legacy PFAS levels remain high in the upper reaches of the Cape Fear River watershed. We agree that one possible reason is the use of products that were manufactured prior to the phase-out (like stockpiled fire-fighting foam). But there could be other reasons such as use of imported products that contain legacy PFASs.

7. L159-163: *I'm wondering what's the contact time of ozonation at that drinking water treatment plant? I'm not entirely sure about the statement here. Could it be possible that such differences in concentrations observed were rather caused by different contact time at different steps? My guess is that levels of PFECAs may vary considerably in a day depending on the production processes at that industrial sites. If the contact time of a treatment step is short enough, then it can be expected that concentrations won't change considerably before and after that treatment. But if the contact time is long enough, then it may reflect an average of emissions in the past couple of hours, which might cause certain temporal variation. This point needs to be addressed before drawing conclusions on how each treatment steps influence the concentration of individual PFASs.*

We agree. The contact time during ozonation is on the order of 15 minutes, but the residence time of the entire plant is approximately a day. We added to following additional interpretation to the revised manuscript: "Alternatively, small concentration changes between treatment processes may be related to temporal changes in source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic residence time of the DWTP."

8. L167: What are these three PFECAs used for?

We are not sure whether these compounds are produced for market or whether they are manufacturing by-products. No change was made to the manuscript to avoid speculation.

9. L197-198: I'm not sure about this statement and the results behind that. In Figure 3, the point of PFMOBA is very weird. First of all, it's below 0%, which cannot be. Second, it's lower than both PFMoPrA and PFPrOPrA. As it's written in L186-187, "based on the observations that PFAS adsorption decreases with decreasing carbon chain length". I would rather expect that PFMOBA lies between PFMoPrA and PFPrOPrA, and doubt that it's an artefact in the experiment. Thus, I would recommend the experiment of PFMOBA be repeated.

The PFMOBA removal percentage is below 0 because of the variability in the analytical method. Experiments were conducted in duplicate, and similar patterns were observed at the other two PAC doses. Most likely, the initial PFMOBA concentration was underestimated. Variability in the +/-20% range is normal for LC-MS/MS analyses. The following sentence was added to the manuscript: "There was no meaningful removal of PFMOBA and PFMoPrA, and the variability shown in Figure S5 is most likely associated with analytical variability."

10. L199-203: This comparison doesn't make sense. Perfluoroalkyl ether chain is a chain itself, and you can't just compare the number of perfluorinated carbons. The ether linkage contributes to the physicochemical properties of the molecule for sure, e.g., via increased molecular size, changed polarity, etc. This comparison can be removed.

I don't mind removing this part and I actually like the other way of counting chain length better. But then we also need to edit the abstract since the abstract is written in this interpretation.

Commented [DK8]: Let's decide based on word count. I still think that this is a reasonable alternative approach – i.e. to make a comparison based on # of perfluorinated carbons alone. Deleting these lines would not affect the abstract.

11. L213-217: This sentence doesn't make sense. From the basic theory of chemistry, one can already know that PFECAs have different physicochemical properties from PFCAs because the structural differences between these molecules. The question is how different, which is the actual thing approved by the experiments here. The sentence here needs to be reformulated to reflect our knowledge about chemistry is not zero.

I want to wait until we decide how to address the comment above to see how we will talk about the impact of structure change on physicochemical properties.

Commented [DK9]: I agree with the reviewer. We can create some space here by not stating something very obvious.

Commented [M10R9]: Delete the whole paragraph? That makes us -50 words lower than the word limit, but counting the title paper.

Commented [DK11R9]: I added a few things. In essence, we already discuss earlier how the addition of ether groups affects adsorbability. See comments I made in manuscript.

Commented [M12R9]: We are at 3024 words without title page, without removing this part or the part in comment #10.